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Fast dynamics of a fragile glass former by time-resolved spectroscopy

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ABSTRACT

We measured the dynamics of the fragile glass former *m*-toluidine in its supercooled phase by the time-resolved optical Kerr effect. Using an experimental time filtering of the internal molecular vibrations a better insight into the fast relaxation processes has been achieved. We analysed the dynamic features of these fast processes and compared them with the mode-coupling theory predictions.

§ 1. INTRODUCTION

The study of the dynamic properties of the supercooled liquids as they supercool and approach the glass transition involves effects that span a very broad range of times and frequencies. The prominent feature of the supercooled liquids is the enormous slowing down of the structural relaxation processes with decreasing temperature. This slowing down is mainly seen in the macroscopic observables, such as the viscosity and long-time diffusion, but it could modify some aspects of the microscopic properties. Experimental study of the fast dynamics in glass formers can provide interesting information about the microscopic dynamics and their interaction with the slower critical processes.

Mode coupling theory (MCT) (Götze 1991, Götze and Sjögren 1992), enabled a remarkable interpretation to be proposed for the dynamics of supercooled fragile liquids based on density fluctuations and this theory describes the liquid–glass transition as one from an ergodic liquid state to a non-ergodic ideal glassy state. This dynamic critical transition, at which the singularity is expected to occur, appears at a temperature T_c higher than T_g . MCT is able to characterize a broad range of time scales, from picoseconds to the longest decay times, associated with the complete structural relaxation, and it provides detailed predictions of the relaxation behaviour of supercooled liquids. These theoretical predictions have triggered many recent experiments, including a specific interest in the short time scale (picoseconds to nanoseconds) and the high-frequency range (gigahertz to terahertz). Most of the experimental methods used to study fast dynamics are frequency-domain techniques, such as light scattering (LS) (Götze 1999). Time- and frequency-domain experiments

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yield the same dynamic information; however, in practice, different aspects of the dynamics can be emphasized by studying the relaxation processes in the two domains (Franosch *et al.* 1997).

In figure 1 we show a typical dynamic spectrum for a molecular glass former in its supercooled state. Clearly several dynamic regimes are demonstrated: the slow dynamics, appearing in the spectra as a peak located around 1 GHz, usually called the α regime, and the fast dynamics, typically located in a frequency range from 10 GHz to 3 THz. This dynamic region can be subdivided into an intermediate region, usually called the β regime (or the β fast regime to distinguish it from the β slow regime present in many dielectric spectra), where a minimum appears, and a high-frequency part where the so-called 'boson peak' and 'microscopic peak' appear. Finally, around 6 THz, intramolecular vibrations are observable. Of course a sharp separation between these dynamic regions does not apply, producing a real complication in their experimental identification and theoretical interpretation. The fast dynamic region is particularly interesting owing to the still unclear nature of its physical properties. For example the boson and microscopic peaks are quite universal features of glass formers but their interpretation is an open problem still. Also the 'schematic model' of MCT, which is able to reproduce properly the α regime and β regime, does not expect a double-peak feature in the high-frequency region (Götze 1991, Götze and Sjögren 1992). So the real molecular glass-forming liquids always exhibit complex dynamics which have not yet been completely addressed. The intramolecular and intermolecular low-frequency

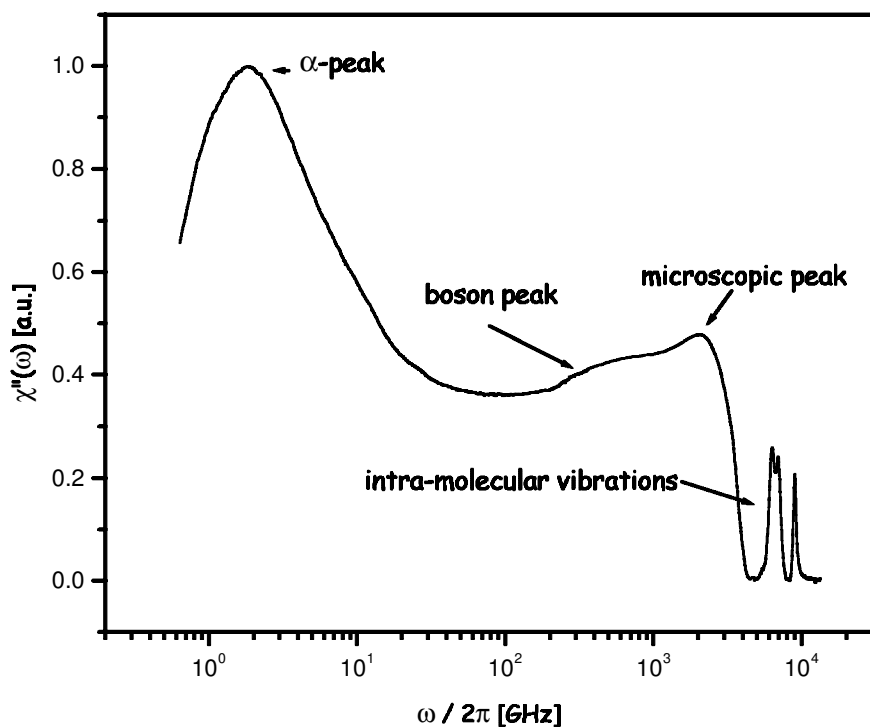


Figure 1. Typical frequency spectrum of a molecular glass-forming liquid.

modes could be very important parameters not yet incorporated into the glass transition theories.

Performing measurements of the overall dynamics of a given glass-forming liquid over a very large time or frequency range, and comparing those results with the MCT predictions may help to answer the following questions. Do those additional features (boson and microscopic modes) in the real glass-forming liquids mask or modify the signature predicted by the schematic model MCT? If this is not the case, to what extent do the measured dynamics agree with the predictions of this theory? Further, do the measurements in the time domain improve the disentanglement of different relaxation processes?

In this framework, we present a study of the fast dynamics of a simple fragile glass former, *m*-toluidine, directly in the time domain over a broad temperature range (including the supercooled liquid state) measured by means of the heterodyne-detected optical Kerr effect (HDOKE) technique.

§ 2. THEORETICAL BACKGROUND

Usually the dynamics of glass-forming liquids are studied in a wide frequency domain (from 1 GHz to about a few terahertz) by LS experiments, covering the whole high-frequency region that includes the boson and microscopic peaks. Nevertheless, very often, the analysis of LS data does not consider the high-frequency range and the theoretical interpretation is based on the asymptotic solutions of MCT schematic model which can be written in a relatively simple analytical form (Götze 1999). To take into account the short-time or high-frequency dynamics properly, a more complete MCT solution has to be considered.

The MCT in the so-called ‘ F_{12} schematic model’, where only a single correlator and the first two terms in the memory expansion are taken into account, predicts that the dynamic correlator $\phi_{q_0}(t)$ would be the solution of the following integro-differential equation (Götze 1991, Götze and Sjögren 1992):

$$\frac{\partial^2}{\partial t^2} \phi_{q_0}(t) + \nu_0 \frac{\partial}{\partial t} \phi_{q_0}(t) + \Omega_0^2 \phi_{q_0}(t) + \Omega_0^2 \int_0^t m_{q_0}(t-t') \frac{\partial}{\partial t'} \phi_{q_0}(t') dt' = 0, \quad (1)$$

$m_{q_0}(t)$ being the memory function, which is a second-order polynomial in $\phi_{q_0}(t)$:

$$m_{q_0}(t) = \lambda_1 \phi_{q_0}(t) + \lambda_2 \phi_{q_0}^2(t). \quad (2)$$

The function $\phi_{q_0}(t)$, obtained by numerical solution of equation (1), is characterized, in the short time, by a damped oscillation (frequency Ω_0 and damping ν_0) that merges in a two-step relaxation pattern called the β regime and α regime, appearing at intermediate and long-time scales respectively. The susceptibility $\chi''_{q_0}(\omega)$, obtained from the $\phi_{q_0}(t)$ correlation function, can be directly compared with frequency measurements, for example the LS experiment. The $\chi''_{q_0}(\omega)$, calculated from the F_{12} model, is able to fit the low-frequency-peak α regime and the intermediate-minimum β regime of the spectra. Concerning the high-frequency region this susceptibility can describe only partly the spectral features. In fact, in this region, the spectra is characterized by the presence of a large spectral band due to the microscopic peak and to a hump localized between the minimum and the microscopic peak, called the boson peak (see figure 1): $\chi''_{q_0}(\omega)$ shows a microscopic peak but is unable to reproduce the hump. So to analyse in detail the short-time or high-frequency dynamics, more sophisticated models are needed.

Alba-Simionesco and Krauzman (1995) and Krakowiack *et al.* (1997) proposed a ‘two-correlator’ MCT model to fit the LS data. They utilized a schematic model with two correlators $\phi_{q_0}(t)$ and $\phi_{q_1}(t)$. The correlator $\phi_{q_0}(t)$ is a solution of an integro-differential equation such as equation (1), while the correlator $\phi_{q_1}(t)$ is the solution of the coupled equation:

$$\frac{\partial^2}{\partial t^2} \phi_{q_1}(t) + \nu_1 \frac{\partial}{\partial t} \phi_{q_1}(t) + \Omega_1^2 \phi_{q_1}(t) + \Omega_1^2 \int_0^t m_{q_1}(t-t') \frac{\partial}{\partial t'} \phi_{q_1}(t') dt' = 0, \quad (3)$$

where the memory function of the correlator $\phi_{q_1}(t)$ is directly proportional to the memory of the correlator $\phi_{q_0}(t)$:

$$m_{q_1}(t) = r m_{q_0}(t). \quad (4)$$

The response function $\chi''_{q_0,q_1}(\omega)$, obtained by Fourier transformation of the quadratic sum of two correlators, has been used to fit LS experiments data on *m*-toluidine at different temperatures in a frequency region from 150 GHz to 4 THz. This model reproduces properly the spectra in the high-frequency region, fitting in a very accurate way the microscopic and boson peaks. Furthermore the fit gives the correct values of the characteristic MCT parameters of system: λ and T_c . Nevertheless this is a very flexible model with a high number of parameters (Ω_1 , ν_1 , Ω_0 , ν_0 , λ_1 , λ_2 , r and the relative weight of the two modes γ) which allows for a good numerical fit easily but which loses direct physical insight.

A ‘slave-correlator’ MCT model was proposed by Sjögren (1986) and used by Franosch *et al.* (1997) to fit the LS spectra. Its equation of motions are as follows: the first is like equation (1), and the second like equation (3) with the ‘slave-correlator’ functions $\phi_{q_s}(t)$, Ω_s , ν_s and $m_{q_s}(t)$ respectively. The memory function $m_{q_s}(t)$ is specified by a single coupling constant r as a quadratic expression $m_{q_s}(t) = r \phi_{q_0}(t) \phi_{q_s}(t)$, where $\phi_{q_0}(t)$ is the solution of equation (1). In this work the spectral susceptibility $\chi''_{q_s}(\omega)$ is obtained from the Fourier transform of the single correlation function $\phi_{q_s}(t)$. This model has been used to fit the experimental spectra of glycerol from 1 GHz to 1 THz. This model is able to reproduce correctly the low-frequency-peak α regime and the intermediate-minimum β regime of the spectra plus the high-frequency region up to about 1 THz. So this model can describe a sort of boson peak feature but is unable to produce the double high-frequency peak, boson and microscopic peaks. This is different from the F_{12} model that reproduces only the microscopic peak.

The previous three MCT models improve the analysis of the spectra allowing us to extend the fitting to the high-frequency region. Nevertheless they introduce several substantial numerical and fitting complications. It is not clear whether these models modify the analysis of the relative low-frequency solutions compared with the simpler MCT asymptotic solutions.

Aoudi *et al.* (2000) studied the *m*-toluidine LS data using both the asymptotic solutions of MCT and the two-correlator MCT model. These workers concluded that the two theoretical models give substantially the same value for the MCT parameters λ and T_c when the analysis is limited to the α and β regimes. According to this study, the boson and microscopic modes do not prevent the region of the minimum in the spectra susceptibility from being analysed.

In previous work (Torré *et al.* 1999, 2000), the high-temperature dynamics of *m*-toluidine have been studied in the time domain by HDOKE experiments and a detailed comparison with the MCT asymptotic solution has been worked out. It has

been found that the α dynamics and the slow part of the β dynamics, the von Schweidler dynamics, are clearly detected and analysed in this time-domain experiment with a better insight than the frequency-domain experiments. Concerning the fast dynamics it has been pointed out how the presence of the intramolecular oscillating contributions in the signal produces a large uncertainty in the analysis of the β regime when the simple interpolation law is used (Torre *et al.* 1999). In contrast, the introduction of the full β correlator function improves the data analysis substantially (Torre *et al.* 2000). However, the presence of a ‘critical relaxation’, which should appear in a very-short-time region as a power-law decay, could not be revealed directly. This relaxation corresponds, in frequency space, to the rising edge of the minimum towards the microscopic peak which very often overlaps with the boson peak.

In the present work we focus on the comparison of the MCT asymptotic solutions with the *m*-toluidine fast dynamics at low temperatures.

§ 3. EXPERIMENTAL ASPECTS

The present study was performed on *m*-toluidine ($\text{CH}_3\text{--C}_6\text{H}_4\text{--NH}_2$), a disubstituted benzene ring with the --CH_3 and --NH_2 groups in the 1,3 positions; it is one of the simplest fragile liquids, which remains very easily supercooled to its thermodynamic glass transition temperature $T_g = 187$ K, while the melting temperature is $T_m = 243.5$ K. Starting with 99% pure *m*-toluidine purchased from Merck, our sample was purified by distillation under vacuum and then kept in a quartz cell of very good optical quality. The cell was placed in a cryostat system, cooled with Peltier cells; this enabled temperature control to better than ± 0.1 K.

In a transient HDOK experiment the signal can be written as (McMorrow *et al.* 1988, Lotshaw *et al.* 1995)

$$S(\tau) \propto \int_{-\infty}^{+\infty} dt I^{\text{probe}}(t - \tau) \int_{-\infty}^{+\infty} dt' R(q, t - t') I_{\text{exc}}(t'), \quad (5)$$

where $I_{\text{probe}}(t)$ ($I_{\text{exc}}(t)$) is the intensity profile of the probe (pump) field and $R(q, t)$ is the response function of the system for a scattering vector of magnitude q . According to the linear response theory, the response function of the system is expressed in terms of the correlation function of the physical observable of the experiment. In an optical Kerr effect (OKE) experiment the measured observable is the anisotropic part of the dielectric constant, so that

$$R(q, t) = -\frac{\theta(t)}{k_B T} \frac{\partial}{\partial t} \Phi(q, t), \quad (6)$$

where

$$\Phi(q, t) = \langle \varepsilon_{xy}(q, t) \varepsilon_{xy}(-q, 0) \rangle.$$

Here, k_B is the Boltzmann constant, T is the temperature and $\theta(t)$ is the Heaviside step function. Note that, in an OKE experiment, the excited anisotropy is characterised by a zero wave-vector, so that we must consider $q \approx 0$ in equation (6). When, as in the present experiment, $I^{\text{probe}}(t)$ and $I^{\text{exc}}(t)$ are very short (less than 100 fs), the convolution product can be neglected in equation (5) and the experiment directly measures the response function

$$S(t) \propto -\frac{\partial}{\partial t} \Phi(t). \quad (7)$$

The imaginary part of the Fourier transform of the HDOKE signal is proportional to data obtained from depolarized LS ($\chi''_{\text{LS}}(\omega)$) (Kinoshita *et al.* 1995):

$$\chi''_{\text{LS}}(\omega) \propto \text{Im} \{ \text{FT}[S_{\text{OKE}}(t)] \}. \quad (8)$$

Our HDOKE measurements were performed at 15 temperatures between 295 and 222 K with an experimental equipment and laser system, which has been presented in detail elsewhere (Bartolini *et al.* 1999). Let us simply recall here that the time resolution allows us to measure the response function by a step-by-step procedure, up to approximately 4 ns.

The amplitude of the HDOKE signal may be detected over a dynamic range of approximately five decades and exhibits a complex relaxation pattern. In figure 2 we show HDOKE signal data on a log-log scale; only ten temperatures out of the 15 measured are displayed for clarity. Each datum is an average of five independent measurements. The measured dynamics exhibit three different regimes: a nearly temperature-independent region from 0.1 to 2–3 ps; an intermediate decay region from 2 to about 10 ps, depending on the temperature; and the final long-time relaxation. The long-time dynamics have a stretched-exponential form with decay times increasing with decreasing temperature. All the data sets have the same general form, but these major features (the three regimes) occur on different time scales depending on the temperature. Data sets were collected from the shortest times through the stretched-exponential decay. In this work we shall analyse only the fast dynamics (from 0.1 to about 10 ps); the slow dynamics will be studied in a subsequent paper.

When HDOKE experiments are performed with very short pulses (60 fs), (see figure 2 and also figure 4 later), the structure of the signal in the fast time region is complex. There is an evident, weakly damped oscillatory contribution, lasting up to about 2–3 ps, which has to be attributed to the intramolecular vibrations; there are

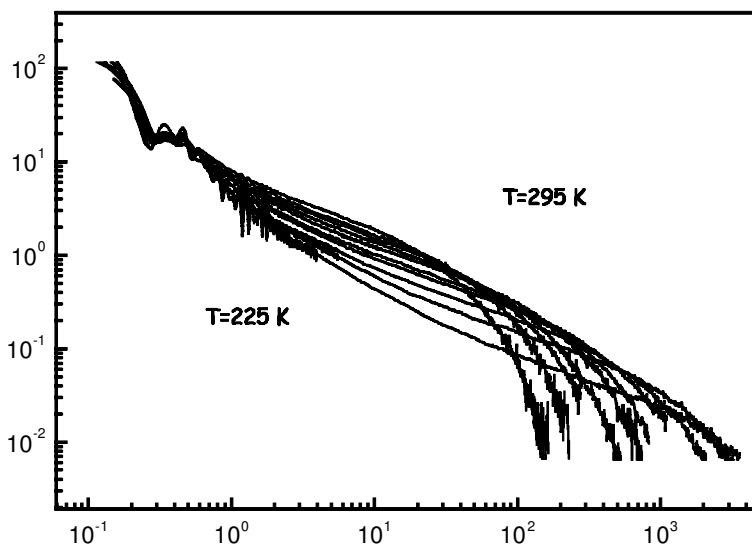


Figure 2. HDOKE signal for $T = 225, 229, 235, 244, 250, 255, 260, 273, 280$ and 295 K.

also strongly damped oscillations that take place in a even faster time region; overall these oscillatory behaviours lie on a decay pattern. The strongly damped oscillations could be attributed to the microscopic and boson dynamics and the relaxation to the fast part of the β regime, the so-called ‘critical decay’. The presence of all these dynamic contributions make the analysis of the HDOS signal at short times particularly difficult. Of course, the removal of the oscillation in the data will be useful to analyse properly the relaxation pattern in the time domain. To achieve this goal a numerical procedure has been recently used (Hinze *et al.* 2000). The time-domain data have been Fourier transformed into the frequency domain, and the resulting frequency-domain data were numerically modified using a Gaussian-shaped filter that cut out the peaks occurring at the frequencies of the oscillations. The filtered data were back Fourier transformed. If the time domain is very extended, as in the present case, these numerical procedures often give unsafe results because some uncontrolled effects show up.

In the present work we apply experimental skill to reduce the oscillations directly in the HDOS data without using any numerical procedure. If we change the time length of the laser pulses used in HDOS experiments, we can selectively intensify the different dynamics contribution in the signal, reducing strongly the intramolecular signal. In fact, short pulses of duration 70 fs or less are able to excite internal molecular vibrations by the stimulated Raman effect since their corresponding bandwidth is large enough to reach the Raman-active intramolecular vibrations. If the pulse duration is stretched to longer durations, the effective bandwidth is reduced and the higher-frequency dynamics can be cut out so that they do not contribute to the signal.

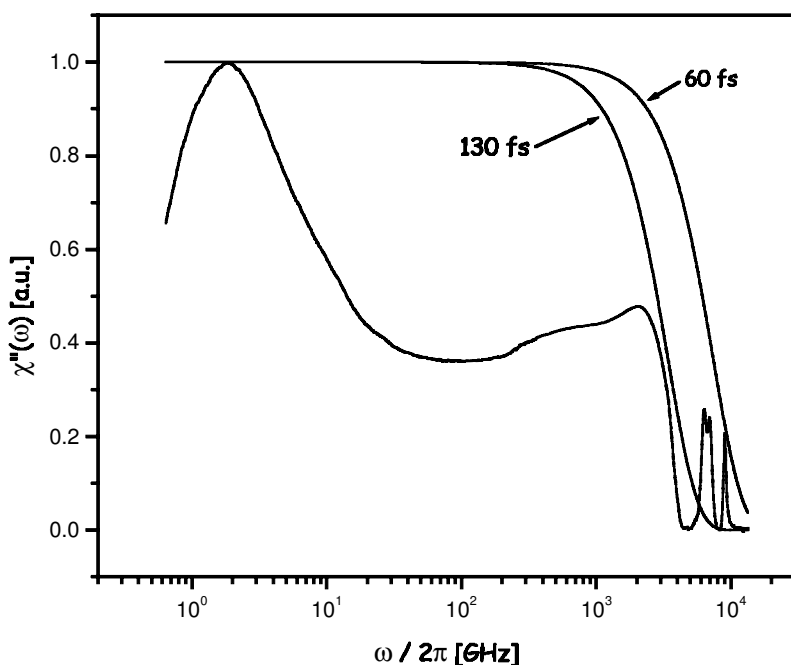


Figure 3. Frequency spectra of a glass-forming liquid and the Fourier transform of the autocorrelation of pulse intensity, taken to be of Gaussian shape, at different pulse lengths, 60 and 130 fs respectively.

In order to measure the dynamics without the intramolecular contribution, we performed measurements with significantly longer pulse lengths, about 130 fs. These pulses do not excite the internal vibrations as we can see in the figure 3 where the Fourier transform of the instrumental response (autocorrelation function of the laser pulse intensity profiles) corresponding to two pulse lengths is reported.

§4. RESULTS

Figure 4 displays the short-time portion of the data at low temperatures ($T \leq 250$ K) obtained using a pulse length of 60 fs on a log-log scale. The curves have been offset on the vertical axis for clarity of presentation. As shown in the figure, oscillations contribute to the HD-OKe signal up to 3 ps. These oscillations excited by stimulated Raman scattering are almost temperature independent in both frequency and amplitude and they are related to intramolecular low-frequency vibrational modes of *m*-toluidine at $\nu \approx 220$, 240 and 300 cm^{-1} . In agreement with the previous work (Torre *et al.* 2000) we found that the simple interpolation law does not allow us to perform a safe fit of the data and the full β correlator function is needed. So in figure 4 we show the time derivative of the full β correlator, obtained by a numerical calculation of the MCT scaling equation of motion (Cummins *et al.* 1997), made following the same method as given by Torre *et al.* (2000). At high tempera-

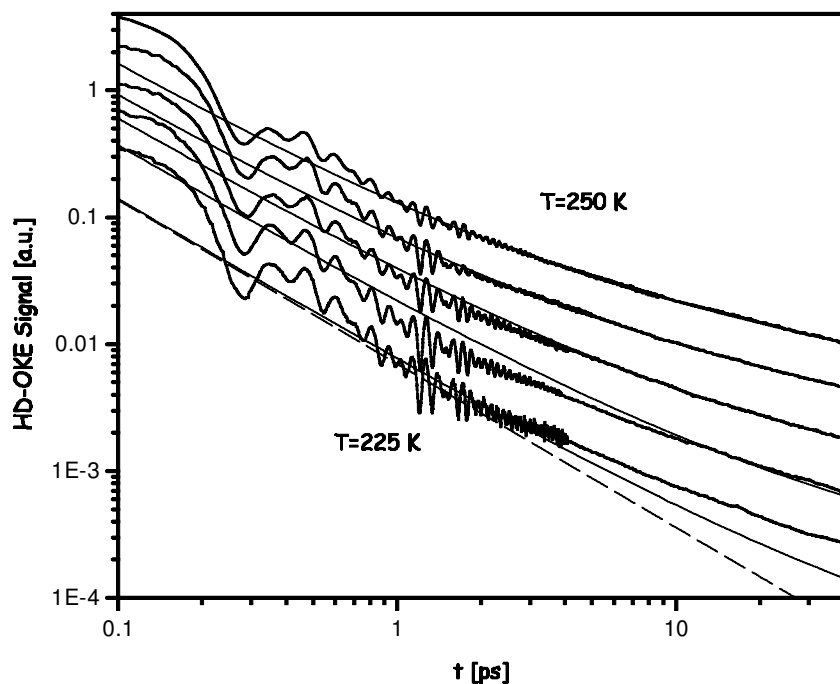


Figure 4. The short-time portions of several data sets (225, 229, 235, 244 and 250 K from bottom to top) on a log-log scale. Oscillations from intramolecular vibrations (6.6, 7.2 and 9 THz) contribute to the HD-OKe signal up to 3 ps. The solid curves are the fit of the OKE data according to the derivative of a full β correlator function with $\lambda = 0.77$ and $T_c = 220$ K. For $T = 225$ K we reported the derivative of a full β correlator, for the same λ and T_c parameters, together with the critical decay indicated by the broken curve.

tures $T > 235$ K, the shape of the full β correlator shows outstanding agreement with the data over the full range of times from 2–3 ps up to tens of picoseconds, predicting $\lambda = 0.77$ and $T_c = 220$ K. These data confirm the ability of the asymptotic solution of ideal MCT to reproduce the glass-former dynamics. However, the critical decay, the short-time leading-order asymptotic solution of the β regime, cannot be identified independently also at low temperatures where it could be well separated from the other leading-order asymptotic solution, the von Schweidler decay. In fact in figure 4 we report the expected critical power law (the dotted curve is a plot of this function with $a = 0.29$, the critical exponent obtained by $\lambda = 0.77$) and it cannot safely assigned to any part of the HD-OKe signal. Furthermore for the lowest temperature $T \leq 235$ K, approaching the estimated critical temperature T_c , the full β correlator does not agree with the data any longer. Indeed, according to the ideal MCT, approaching T_c the structural time scales should go to infinity and the structural relaxation should cease. Clearly these predictions are not in agreement with the data. So, in the range of temperatures near and below T_c , the ideal MCT is not appropriate any longer and the extended MCT model must be used.

In order to obtain better insight into the fast dynamics we performed measurements with the longer pulse (130 fs). For clarity of presentation, only some of the whole range of temperatures are shown in figure 5. The signals obtained with short- and long-pulse experiments agree perfectly, of course, apart from the fast intramolecular contributions. The data taken with the longer pulse do not show the intramolecular oscillations any longer but an oscillation of about 200 fs period

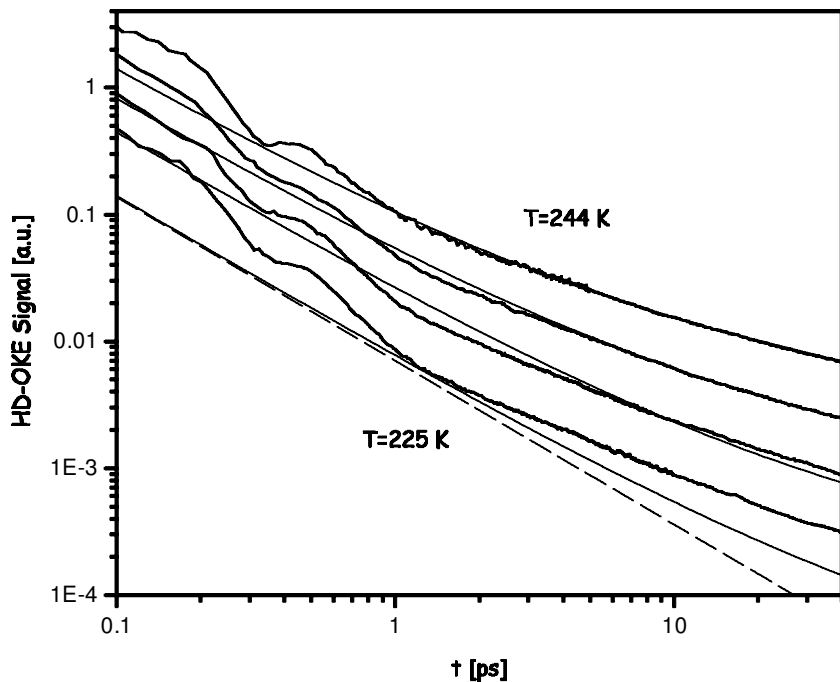


Figure 5. The short-time part of the data at 225, 229, 235 and 244 K obtained with a pulse length of 130 fs. No intramolecular oscillations are present. Also reported is the derivative of a full β correlator function for $\lambda = 0.77$ and $T_c = 220$ K and the critical decay indicated by the broken curve.

is left. This oscillating contribution to the signal corresponds to double-peak features present in the high-frequency region, so it has to be attributed to the microscopic and boson dynamics. Indeed it should be mainly constituted by the microscopic dynamics. Anyway the data show clearly that these oscillations are slightly temperature dependent and they are strongly damped; so their effect is substantially negligible after 1 ps.

In figure 5 we compare the previous time derivative of the full β correlators with the new data; again we found excellent agreement for $T > 235$ K but clear disagreement when $T \leq 235$ K. Using an adapted longer pulse in the HDOKE experiment, it has been possible to extend at faster times (less than 1 ps) the visibility of pure relaxation processes, free from oscillating contributions; nevertheless the critical decay does not show up and it is still not separated from the von Schweidler decay, even in data at lower temperatures.

In order to understand whether the extraction of the MCT parameters is improved by removing the intramolecular dynamics, we test the simple interpolation law on these new data. So we fit the data at 235 K with the interpolation law in the fitting range 1–100 ps. The fit performed with the two scaling exponents a and b constrained by the equation that links them to the exponent parameter (Torre *et al.* 1999) found that $a = 0.295 \pm 0.01$, in very good agreement with the full β correlator fitting results. When the scaling exponents, are not constrained, we found that $a = 0.26 \pm 0.04$ and $b = 0.54 \pm 0.02$, again in good agreement with the previous results. This last result is quite important since usually the interpolation formula with free scaling exponents does not yield coherent results, that is the exponent parameters do not verify the expected constraining equation. Furthermore it shows how the extension of the fitting range, obtained by removing the intramolecular oscillation, is able to fix the critical parameter a correctly even if the critical decay does not appear directly in the data. At present a complete study of the fast dynamics according to the introduced MCT models and to the extended MCT is in progress in our research group.

As a final remark we would like to stress the main results of this work. The previous analysis of HDOKE data on *m*-toluidine suggests that the dynamic contributions of microscopic and boson modes to the structural relaxation processes cease on a very fast time scale (less than 1 ps) for any temperatures, so that the simple asymptotic results of the schematic MCT can correctly describe the glass-former dynamics in such extended time and temperature ranges.

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